# Indirect Relativistic Effect on the 5$f$ Electrons in Uranium†

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Hartree nonrelativistic atomic wave functions have been calculated for elements 89 through 98. The eigenvalues $|\mathcal{E}|$ of the 5$f$ and 6$d$ electrons in uranium were, respectively, 5.69 and 1.06 eV greater than those in the relativistic calculation by Cohen. The energy difference between the 5$f$ and 6$d$ eigenvalues is 4.6 eV greater in the nonrelativistic calculation. Since both the 5$f$ and 6$d$ bands are expected to be partially occupied in metallic uranium and neighboring elements, it is suggested that the results of solid-state calculations for the actinide elements using nonrelativistic crystal potentials will not be even qualitatively correct.

THE authors have calculated nonrelativistic ($NR$) wave functions without exchange on an IBM 7090 for elements 89 through 98 for various configurations of the neutral free atom. The program was checked by reproducing the results obtained by Ridley[1] for $_{92}U^{+6}$. We are now engaged in calculating the corresponding relativistic ($R$) wave functions and have modified the $NR$ program for this purpose. When the calculations have been completed, details will be published in one or more Los Alamos Reports.

The only $R$ calculation presently available for atomic numbers greater than 80 was done by Cohen[2] for uranium. Preliminary comparison of his $R$ eigenvalues with our $NR$ eigenvalues leads to the conclusion that strictly $NR$ calculations will not yield meaningful descriptions of the chemical and solid-state behavior of the actinide elements.

Table I contains the $NR$ and $R$ energy eigenvalues (expressed in ry) for some of the electrons of $_{92}U$ in the ground-state configuration, $5f^36d7s^2$. The ratio $R/NR$ is included to show the magnitude and direction of shifts in energy levels. The center of gravity of levels split by the spin-orbit interaction was taken for $R$ where both energies were available.

TABLE I. Comparison of relativistic and nonrelativistic energy eigenvalues (in rydbergs) for neutral uranium.

| $nl$ | $j$ | Eigenvalue $E(nl)$ $NR$ | $R$ | Ratio $R/NR$ |
|---|---|---|---|---|
| 5$s$ | $\frac{1}{2}$ | 17.53 | 22.62 | 1.29 |
| 5$p$ | $\frac{1}{2}$<br>$\frac{3}{2}$ | 13.91 | 18.11<br>14.11 | 1.11 |
| 5$d$ | $\frac{3}{2}$<br>$\frac{5}{2}$ | 7.64 | 7.58<br>7.00 | 0.95 |
| 5$f$ | $\frac{5}{2}$<br>$\frac{7}{2}$ | 0.692 | 0.274<br>··· | 0.40[a] |
| 6$d$ | $\frac{3}{2}$<br>$\frac{5}{2}$ | 0.303 | 0.225<br>··· | 0.74[a] |
| 7$s$ | $\frac{1}{2}$ | 0.311 | 0.379 | 1.22 |

[a] If both $j$ states were occupied, the ratio would be smaller.

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[1] E. C. Ridley, Proc. Roy. Soc. (London) **A243**, 422 (1958).

[2] S. Cohen, Atomic Energy Commission Report AECU-4117 or University of California Radiation Laboratory Report UCRL-8633, 1959 (unpublished).

Note the regular variation of $R/NR$ as a function of $l$ in the $n=5$ shell. The electrons of lower angular momentum are bound more tightly in the $R$ calculation, and, hence, they shield the nuclear charge more effectively. This causes the electrons of higher angular momentum to be bound more loosely. The same effect is present in other electron shells. This indirect relativistic effect was apparently first noticed by Mayers[3] for the 5$d$ electrons of mercury, although there the shift is relatively small.

The 5$f$ eigenvalue is changing rapidly as a function of $Z$ throughout the actinide sequence and is very sensitive to small changes in the atomic potential. Therefore, the 5$f$ energy shift in $_{92}U$ is unusually large: more than 5 eV. Although the 6$d$ energy shift is in the same direction, it is much smaller. The difference between energy levels $6d-5f$ is 0.67 eV in the $R$ calculation and 5.29 eV in the $NR$ calculation, yielding a net change in energy difference of 4.6 eV.

Since in metallic uranium both the 5$f$ and 6$d$ bands are expected to be partially occupied, we need to know the relative positions of these bands within an error of much less than 5 eV. Evidently relativistic effects cannot be ignored.

It seems likely that since the relativistic effect on the 5$f$ and 6$d$ electrons is indirect, it will be satisfactory, in solid-state calculations involving actinide elements, to calculate the crystal potential relativistically and then treat the 5$f$ and 6$d$ electrons in the usual way.

Platinum is the only other element with two competing incomplete shells (configuration $5d^96s$) for which an $R$ calculation is available.[4] We did an $NR$ calculation, since (apparently) none was available in the literature

TABLE II. Comparison of relativistic and nonrelativistic energy eigenvalues (in rydbergs) for neutral platinum .

| $nl$ | $j$ | Eigenvalue $E(nl)$ $NR$ | $R$ | Ratio $R/NR$ |
|---|---|---|---|---|
| 5$d$ | $\frac{3}{2}$<br>$\frac{5}{2}$ | 0.601 | 0.599<br>0.486 | 0.88 |
| 6$s$ | $\frac{1}{2}$ | 0.395 | 0.502 | 1.27 |

[3] D. F. Mayers, Proc. Roy. Soc. (London) **A241**, 93 (1957).

[4] S. Cohen, Rand Corporation Research Memorandum, RM-2405—AEC, 1959 (unpublished).

TABLE III. Ratio of $R$ to $NR$ eigenvalues (in rydbergs) for several electron shells.

| | $1s$ | $4f$ | $5d$ | $6s$ |
|---|---|---|---|---|
| $_{26}$Fe | 1.008 | ... | ... | ... |
| $_{74}$W | 1.09 | 0.81 | 0.84[a] | 1.16 |
| $_{78}$Pt | 1.10 | 0.86 | 0.88 | 1.27 |
| $_{80}$Hg | 1.11 | 0.87 | 0.84 | 1.20 |
| $_{92}$U | 1.15 | 0.91 | 0.95 | 1.34 |

[a] Center of gravity not known, since only one $j$ state is occupied.

for comparison. In Table II we list the $R$ and $NR$ eigenvalues for the incomplete 5d and 6s shells.

Taking the center of gravity of the two $5d$ levels, we find the difference of energy levels $6s-5d$ to be 0.39 eV in the $R$ calculation and 2.80 eV in the $NR$ calculation, yielding a net change in energy difference of 2.4 eV. The energy shifts are similar to those in uranium, though not as large.

Parenthetically it may be remarked that, for both elements, the $R$ results are more reasonable than the $NR$, since we expect the eigenvalues of two competing incomplete shells to be close together, and this was true for the $R$ results but definitely not for the $NR$ results.

Cohen did $R$ calculations not only for $_{92}$U and $_{78}$Pt, but also[5–7] for $_{80}$Hg, $_{74}$W, and $_{27}$Fe. $NR$ calculations for these elements were available in the literature,[8–10] but since those for $_{80}$Hg and $_{74}$W were more than 25 years old, we carefully recomputed them. The accuracy achieved by Hartree and Hartree in their results for $_{80}$Hg was remarkable, considering that only desk calculators were available to them in 1935. In Table III we list the $R/NR$ ratios for the $1s$, $4f$, $5d$, and $6s$ electrons, to show how the relativistic effects vary with $Z$.

Apparently the indirect relativistic effect on electrons of high angular momentum is stronger when those electrons are near the surface. It would be worthwhile to do $NR$ and $R$ calculations for $_{64}$Gd in the ground-state configuration $4f^75d6s^2$ to determine whether or not the shifts in the $4f$ and $5d$ energy levels are significant for the rare earths.

[5] S. Cohen, Rand Corporation Research Memorandum, RM-2272—AEC, 1958 (unpublished).
[6] S. Cohen, Phys. Rev. **118**, 489 (1960).
[7] S. Cohen, Rand Corporation Research Memorandum, RM-2406—AEC, 1959 (unpublished).
[8] D. R. Hartree and W. Hartree, Proc. Roy. Soc. (London) **A149**, 210 (1935).
[9] M. F. Manning and J. Millman, Phys. Rev. **49**, 848 (1936).
[10] F. Stern, Phys. Rev. **104**, 684 (1956).

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# Polarization of Optical Radiation Induced by Electron Impact on Helium*

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An investigation of the polarization of the atomic line radiation induced by electron impact on helium has been undertaken. Experimental data have been obtained on the polarization of several lines as a function of both electron energy and pressure. Secondary excitation processes, such as collision of the second kind and radiative transfer (cascade), are found to play an important role in the polarization. Expressions are derived for the analysis of the pressure effects on the polarization. Gas-kinetic collision cross sections involving atoms in excited states have been determined by observing the depolarization as the gas pressure increases.

## INTRODUCTION

IF an excitation mechanism, such as electron impact or absorption of polarized resonance radiation, can simultaneously excite and orient an atom with respect to a given direction, then the radiation emitted when the atom de-excites can exhibit polarization.

In particular, consider the polarization of the light excited by a well-collimated beam of monoenergetic electrons. The quantity termed the polarization, $P$, is defined through the equation

$$P=(I_{\parallel}-I_{\perp})/(I_{\parallel}+I_{\perp}),$$

where $I_{\parallel}$ and $I_{\perp}$, in an observation direction perpendicular to the beam, are intensities of the radiation with the electric vectors, respectively, parallel and perpendicular to the beam direction.

The phenomenon of the polarization of atomic radiation induced by electron impact can most easily be understood qualitatively by considering Lamb's example[1] of a spinless hydrogen atom in the $1s$ ground state being struck by a spinless electron. If the bombarding electron energy is the threshold energy for exciting the $2p$ state and the electron succeeds in exciting the $2p$ state, then this electron (or exchanged electron) comes to rest. The linear momentum imparted to the

* Supported by the Air Force Office of Scientific Research.
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[1] W. E. Lamb, Phys. Rev. **105**, 559 (1957).